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Relationships between Polyurethane Elastomer Structure and Ageing Properties: Part 4: Effect of Di-isocyanate

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SUMMARY

The final report in the present series of investigations describes the effect of varying the di-isocyanate on the ageing properties of polyurethane elastomers.

Polyester and polyether urethane elastomers were prepared with selected di-isocyanates and crosslinked and/or chain extended with either 1,1',1"-trimethylol propane (TMP) or mixtures of TMP and 4,4'-methylene-bis-(2-chloroaniline), MOCA. Elastomers prepared with toluene di-isocyanate (TDI) gave the most satisfactory initial properties and resistance to ageing in dry air at 80°C, water at 22 and 80°C, and STF (petrol) at 65°C.

None of the elastomers prepared from the other di-isocyanates examined including 1,4-naphthalene, 4,4-diphenyl methane, 1,6-hexamethylene, 4,4-methylene bis-cyclohexyl, trimethylhexamethylene, isophorone, and xylene had equally satisfactory all round properties to those based on TDI. Further disadvantages of these di-isocyanates were their extremely high or low reactivities, high cost and limited availability compared to TDI.

The report also summarises the results of previous investigations in the present series.

Further copies of this technical report can be obtained from Defence Research Information Centre, Station Square House, St Mary Cray, Orpington, Kent. BR5 3RE

CONTENTS

Reference: WAC/213/09

1 INTRODUCTION

Previous reports[1,2,3] in the present series of investigations into the relationships between polyurethane chemical structure and ageing properties have described the effects of varying: (i) the degree of crosslinking, (ii) the backbone polyol and (iii) the chemical group structure in elastomers prepared from typical polyester and polyether/toluene di-isocyanate prepolymers crosslinked and/or chain extended with diols, triols and diamines. The effects of using alternative backbone polyols, for example, hydroxyl-terminated polybutadienes, have also been described previously.[3,4]

These investigations have shown that while unaged polyester urethane elastomers possess superior mechanical properties coupled with rather better resistance to dry air and petroleum (STF) compared with polyether urethanes, the latter have superior hydrolytic stability, but even so polyether urethanes have inferior hydrolytic stability to urethanes prepared from hydroxyl-terminated polybutadienes.

In addition, it has been shown[3] that urethane elastomers cured with diamines, for example, 4,4'-methylene-bis-(2-chloroaniline), MOCA, and blends of MOCA with diols and triols such as 1,1',1"-trimethylol propane (TMP) and 1,4-butane diol (BD) possess superior initial mechanical and ageing properties, especially when they are fairly highly crosslinked, compared to elastomers in which diols or triols are the sole curing agents. The high strength of the MOCA cured elastomers is attributed to the stiffness of the aromatic groups of the MOCA and the stronger interchain attraction of the urea groups and the formation of biuret crosslinks compared with urethane groups.

However, there are some doubts as to the desirability of using MOCA or other halogenated aromatic amines as curing agents for polyurethanes because of possible health hazards (see Note in Appendix A). Therefore it is possible that the use of di-isocyanates with more bulky rigid aromatic structures than toluene di-isocyanate (TDI) might produce elastomers with equally good properties, thus allowing all or part of the MOCA curing agent to be replaced with diol/triols.

Similarly, a number of new aliphatic and cycloaliphatic di-isocyanates have recently become available commercially which are claimed to produce elastomers with enhanced stability to hydrolysis and/or photo-oxidative degradation and were considered worthy of assessment.

The object of the present investigation, the last in the present series, was to study the ageing properties of elastomers of typical polyester and polyether prepolymers prepared with various di-isocyanates, crosslinked and/or chain extended with either triols or triol/diamine blends.

2 MATERIALS AND METHODS OF PREPARATION

All the elastomers were prepared using either (i) a commercially supplied polyester, polyethylene adipate Formrez F7-37 ex-Witco Chemical Co (hydroxyl no 59.0, acid no 0.4, H_2O 0.2%, average molecular weight 1890) or (ii) a commercially supplied polyether, polyoxybutylene glycol, 'Polymeg' ex-Quaker Oats Co (hydroxyl no 56.7, acid no 0.01, H_2O, 0.1%, average molecular weight 1980). 1.0 mole equivalent reacted with 2.1 moles equivalent of the di-isocyanates listed in Tables 1 and 2. The polyester or polyether elastomers were crosslinked and/or chain extended either with (i) 0.66 mole equivalent of TMP or (ii) a mixture of MOCA, 0.5 mole equivalent, and TMP, 0.33 mole equivalent.

The methods of preparation summarised in Table 2 are described in Appendix A.

3 EXPERIMENTAL

British Standard type E dumb-bell test pieces (four per test) were cut from the cast sheets and the width and thickness measured before exposure to the test conditions. Dumb-bells, in sets of four, were suspended in loosely stoppered glass tubes and exposed to some or all of the following environments for 28 days:

Controls	Conditioned in air at 20°C
Hot/dry	Suspended in air at 80°C
Hot/wet	Immersed in boiled out distilled water at 80°C
Cold/wet	Immersed in boiled out distilled water at 22°C
*Standard Test Fluid (STF)	Immersed in Standard Test Fluid at 65°C

The charged tubes were placed in circulating air ovens in which the temperatures did not vary by more than ± 0.5°C from the test temperature. After 28 days' exposure the tubes and contents were removed from the oven and conditioned at room temperature for 24 hours before testing. After the conditioning period, the groups of four specimens were removed from the tubes, dried from a superficial liquid, and tested for hardness, moduli, extension at break and tensile strength as quickly as possible. Hardness was measured using a micro-indentometer, and the tensile properties were measured by British Standard Methods [5,6] on a Hounsfield Tensometer. Unaged control specimens cut from the materials were tested by the same methods, and the results used as 'unaged" reference points.

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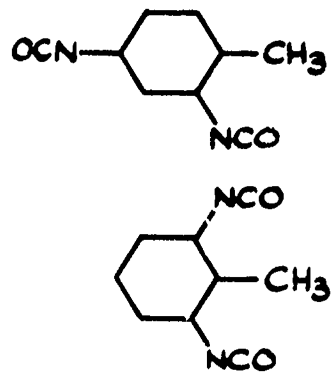
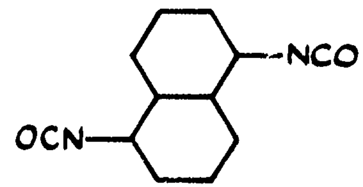
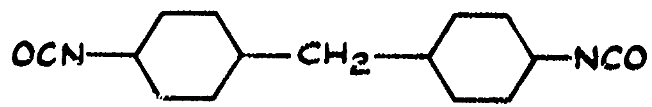
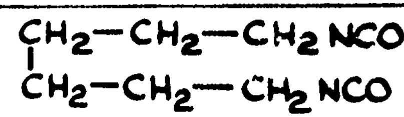
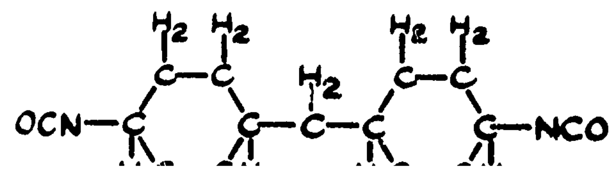
*Standard Test Fluid (STF) consists of a 70/30 v/v mixture of iso-octane and toluene, and is intended to represent a standard "medium to high aromatics" content petrol.[7]

TABLE 1

SELECTION OF DI-ISOCYANATES

Code in Text	Chemical Name and Physical Properties	Chemical Structure	Molecular Weight	Trade Name and/or Supplier
TDI (100)	Toluene di-isocyanate 100% 2,4 isomer (liquid at room temperature)	 2,4 isomer 2,6 isomer	174	Hylene T, DuPont (UK)
TDI (80/20)	Toluene di-isocyanate 80% 2,4 isomer 20% 2,6 isomer (liquid at room temperature)			Hylene TM, DuPont (UK)
TDI (65/35)	Toluene di-isocyanate 65% 2,4 isomer 35% 2,6 isomer (liquid at room temperature)			Hylene TM 65, DuPont (UK)
NDI	1,5-Naphthalene di-isocyanate (solid at room temperature)		210	Desmodur 15, Bayer
MDI	4,4-Diphenyl methane di-isocyanate (solid at room temperature)		250	Desmodur 44, Bayer
MDI (mod)	Probably a 4,4-diphenyl methane di-isocyanate carbodionide eutectic (solid/liquid mixture at room temperature)	as above	288	Isonate 143L, Upjohn
HDI	1,6-Hexamethylene di-isocyanate (liquid at room temperature)		168	Desmodur H, Bayer
MCI	4,4-Methylene bis-cyclohexyl di-isocyanate (liquid at room temperature) 98.5% pure		262	Nacconate H12, Allied Chemicals

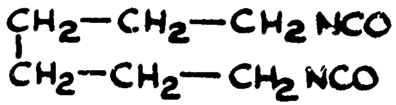
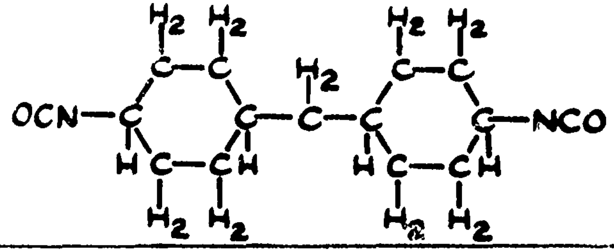
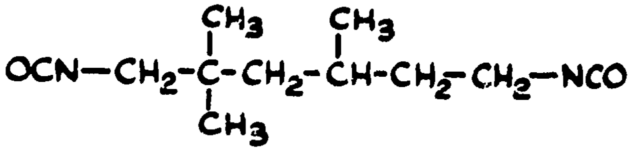
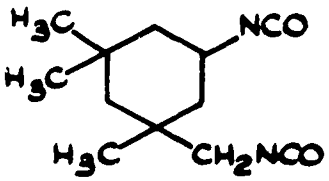
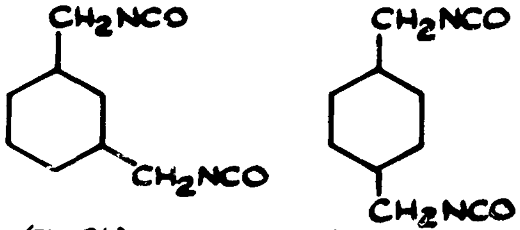
	di-isocyanate (solid at room temperature)			Bayer
MDI (mod)	Probably a 4,4-diphenyl methane di-isocyanate carbodionide eutectic (solid/liquid mixture at room temperature)	as above	288	Isonate 143L, Upjohn
HDI	1,6-Hexamethylene di-isocyanate (liquid at room temperature)		168	Desmodur H, Bayer
MCI	4,4-Methylene bis-cyclohexyl di-isocyanate (liquid at room temperature) 98.5% pure		262	Nacconate H12, Allied Chemicals
TMHDI	Trimethylhexamethylene di-isocyanate (liquid at room temperature)		210	Verba Chemie, AG
IPDI	Isophorone di-isocyanate (liquid at room temperature)		222	Verba Chemie, AG
XDI	Xylene di-isocyanate 70/30 mixture of m- and p-xylene di-isocyanate (liquid at room temperature) 99% pure	 (70%) m- (30%) p-	188	Takenate 500, Takeda, Japan

TABLE 2

CHARACTERISTICS OF POLYURETHANE ELASTOMERS PREPARED WITH VARIOUS DI-ISOCYANATES

Elastomer Code Number	Prepolymer		Processing Conditions		Catalyst	Cross Linker/Chain Extender			Characteristics of Cured Elastomer
	Polyol (1 mole equivalent)	Di-isocyanate (2.1 moles equivalent)	(h)	(Temp °C)		TMP (mole)	TMP (mole)	MOCA (mole)	
S 110	Ethylene adipate av mol wt 1900 (Polyester)	TDI 100	3	80-85	Nil	-	0.33	0.50	good
S 110A		TDI 80/20	3	80-85	"	-	0.33	0.50	good, slightly yellow
S 111A		TDI 80/20	3	80-85	"	0.66	-	-	good, " "
S 111		TDI 65/35	3	80-85	"	-	0.33	0.50	good, " "
S 112A		NDI	1½	130	"	-	0.33	0.50	poor, very rapid cure, partly gelled
S 112B		NDI	1½	130	"	0.66	-	-	fair-good, slightly opaque, a few bubbles
S 113A		MDI	1½	105	"	-	0.33	0.50	fair-poor, very rapid cure
S 113B		MDI	1½	100	"	0.66	-	-	fair, a few bubbles
S 116A		MDI mod	2	105	"	-	0.33	0.50	fair-good, a few bubbles
S 116B		MDI mod	2	105	"	0.66	-	-	good
S 114A		HDI	1	120	"	-	0.33	0.50	flexible but lumpy
S 114B		HDI	1	120	"	0.66	-	-	fair, moderate number of bubbles
S 117A		MCI	3	80-85	"	-	0.33	0.50	good
S 117B		MCI	3	80-85	"	0.66	-	-	slow cure, thermoplastic
S 132A		XDI	3	80-85	"	-	0.33	0.50	good, slightly opaque
S 132B		XDI	3	80-85	"	0.66	-	-	fair-good, rather soft
S 118	Polyoxy-butylene glycol av mol wt 2000 (Polyether)	TDI 100	3	80-85	"	-	0.33	0.50	good, slightly translucent
S 119		TDI 80/20	3	80-85	"	-	0.33	0.50	good, " yellow
S 66		TDI 80/20	3	80-85	"	0.66	-	-	good
S 120		TDI 63/35	3	80-85	"	-	0.33	0.50	good, slightly yellow
S 121A		NDI	1½	130	"	-	0.33	0.50	poor, extremely rapid cure
S 121B		NDI	1½	130	"	0.66	-	-	good
[illegible]		MDI	2	105	"		0.33	0.50	fair, rapid cure, some gel

								bubbles
S 117A		MCI	3 80-85	"	-	0.33	0.50	good
S 117B		MCI	3 80-85	"	0.66	-	-	slow cure, thermoplastic
S 132A		XDI	3 80-85	"	-	0.33	0.50	good, slightly opaque
S 132B		XDI	3 80-85	"	0.66	-	-	fair-good, rather soft
S 118	Polyoxy-butylene glycol av mol wt 2000 (Polyether)	TDI 100	3 80-85	"	-	0.33	0.50	good, slightly translucent
S 119		TDI 80/20	3 80-85	"	-	0.33	0.50	good, " yellow
S 66		TDI 80/20	3 80-85	"	0.66	-	-	good
S 120		TDI 63/35	3 80-85	"	-	0.33	0.50	good, slightly yellow
S 121A		NDI	1½ 130	"	-	0.33	0.50	poor, extremely rapid cure
S 121B		NDI	1½ 130	"	0.66	-	-	good
S 122A		MDI	2 105	"	-	0.33	0.50	fair, rapid cure, some gel particles
S 122B		MDI	2 105	"	0.66	-	-	fair-poor, rivelled surface
S 124A		MDI mod	2 105	"	-	0.33	0.50	fair, rapid cure, ridged surface
S 124B		MDI mod	2 105	"	0.66	-	-	poor, slow cure
S 123A		HDI	2 100	0.05% DBTL*	-	0.33	0.50	good, flexible
S 123B		HDI	2 100	0.05% DBTL*	0.66	-	-	tacky, slow cure
S 125A		MCI	2 100	0.05% DBTL*	-	0.33	0.50	good, flexible
S 125B		MCI	2 100	0.05% DBTL*	0.66	-	-	tacky, slow cure
S 126		TMHDI	3 100	0.05% DBTL*	-	0.33	0.50	good, flexible
S 126A		TMHDI	3 100	0.05% DBTL*	0.66	-	-	very slow cure
S 127		IPDI	3 100	0.05% DBTL*	-	0.33	0.50	good, flexible
S 127A		IPDI	3 100	0.05% DBTL*	0.66	-	-	very slow cure
S 133A		XDI	3 80	Nil	-	0.33	0.50	fair, slightly opaque (crystalline)
S 133B		XDI	3 80		0.66	-	-	soft, very slow cure

*Catalyst: dibutyl tin dilaurate

4 RESULTS

The methods of processing the various elastomers and their condition are summarised in Table 2.

The visual appearance of the elastomers before and after ageing are recorded in Table 12, Appendix B. The mechanical properties of the elastomers are summarised in Table 13, Appendix B, and the percentage changes in the original mechanical properties of the elastomers after ageing are recorded in Tables 3 - 11.

4 1 Selection of Elastomers for Ageing Trials

The general condition and processing characteristics of polyurethane elastomers prepared from various di-isocyanates are described below.

All three grades of TDI proved to be the most versatile of the di-isocyanates examined producing satisfactory elastomers with both TMP/MOCA and TMP, with good processing, casting and curing characteristics.

On the other hand, elastomers prepared with HDI, MCI, XDI, TMHDI and IPDI were usually more satisfactory when cured with TMP/MOCA mixtures than solely with TMP as the latter produced soft undercured elastomers. However, certain polyester prepolymers, especially those prepared with di-isocyanates of high aromatic content, for example NDI and MDI, were extremely reactive towards TMP/MOCA mixtures and gave high exotherms on addition of the curing agent, producing elastomers often of poor surface appearance containing gel particles or air bubbles. The enhanced reactivity of isocyanates containing aromatic groups over aliphatic isocyanates is probably due to the electron attracting nature of the aromatic groups. These particular prepolymers yielded satisfactory elastomers when cured solely with TMP.

The most promising elastomers listed in Table 2 were selected for ageing trials.

4 2 Visual Assessment

The general condition of the polyurethane elastomers judged by visual and empirical methods of assessment are described below.

4 2 1 Initially (Unaged)

All the elastomers prepared from polyesters were strong and tough; those based on TDI 100 and TDI 80 were almost colourless and transparent while those based on TDI 65 were slightly yellow and translucent. Polyester urethane elastomers based on NDI and MDI were slightly brown, those based on HDI were white and opaque, while those based on MCI and XDI were pale yellow.

Polyether urethanes based on TDI, HDI, TMHDI and IPDI were fairly tough, those based on NDI and MDI appeared to be more flexible, while those based on MDI (mod) and MCI were rather weak.

4 2 2 Dry Air (80°C)

After ageing in dry air for 28 days at 80°C all the polyester urethanes showed some discolouration either becoming more yellow or brown. Elastomers based on TDI and MCI showed the least colour change, while those based on NDI were the most seriously affected.

All the polyester elastomers, apart from those based on HDI and XDI, appeared to show some increase in strength.

All the polyether elastomers, especially those based on NDI, became more discoloured and all the elastomers, with the exception of those based on TDI and MDI (mod), appeared to lose strength.

4 2 3 Water Immersion (22°C)

After 28 days' immersion in water at 22°C, which is admittedly a relatively mild condition, none of the urethane elastomers, except for those based on NDI which were more amber, showed any appreciable change of colour or strength. Similarly, apart from elastomers based on XDI which showed severe stress cracking, none of the elastomers showed any appreciable colour change or loss of strength.

4 2 4 Water Immersion (80°C)

Under more severe conditions of immersion in water for 28 days at 80°C all the polyester urethanes were severely degraded; the only materials which were not completely disintegrated and retained any degree of integrity were TMP/MOCA cured polyesters based on TDI and XDI. All the polyether urethane elastomers remained intact. Polyether urethane elastomers based on TDI, NDI, MCI and MDI remained reasonably tough but showed slight or moderate discolouration; those based on TMHDI and IPDI showed virtually no change of colour but were weak. Polyether elastomers based on XDI showed severe stress cracking.

4 2 5 STF(Petrol) Immersion (65°C)

Apart from very slight or slight swelling none of the polyester urethane elastomers appeared to be degraded after 28 days' immersion in STF. On the other hand, the majority of the polyether urethane elastomers were swollen to a slight or moderate degree during immersion in STF and showed apparent losses of strength on recovery. However elastomers based on TMHDI, IPDI and XDI showed severe swelling and loss of strength. None of the elastomers, apart from those based on MDI and NDI showed appreciable colour change.

4 3 Mechanical Properties

4 3 1 Unaged

Tables 3 and 4 show that the initial mechanical properties of polyurethane elastomers cured with TMP/MOCA mixtures were generally better than those

TABLE 3

EFFECT OF DI-ISOCYANATE ON PHYSICAL PROPERTIES OF UNAGED POLYURETHANE ELASTOMERS USING TMP/MOCA CURE

Type of Di-isocyanate	Polyester (Ethylene Adipate)							Polyether (Polyoxybutylene Glycol)						
	Code S No	Tensile Strength, MN/m^2	Extension at Break, %	Modulus at (%)			Hardness, BS°	Code S No	Tensile Strength, MN/m^2	Extension at Break, %	Modulus at (%)			Hardness, BS°
				100	200	300					100	200	300	
TDI 80/20	110 A	36.0	545	2.4	3.1	6.2	85	119	16.9	345	3.0	5.3	9.9	89
NDI	112 A	18.1	390	3.4	6.0	13.1	91	121 A	3.9	120	3.5	-	-	90
MDI	113 A	22.7	420	2.6	5.0	10.0	89	122 A	6.1	215	3.8	6.0	-	90
HDI	114 A	17.9	490	5.4	5.4	7.1	99	123 A	13.6	460	0.8	0.8	1.6	65
MDI mod	116 A	26.2	355	3.8	6.7	16.1	89	-	-	-	-	-	-	-
MCI	117 A	33.2	550	1.3	2.8	6.0	67	125 A	5.0	285	1.0	4.5	-	66
XDI	132 A	30.5	550	2.2	3.3	5.5	97	133 A	18.8	565	1.3	1.9	3.1	82
TMHDI		-	-	-	-	-	-	126 A	5.6	430	0.3	0.8	1.5	57
IPDI		-	-	-	-	-	-	127 A	15.9	445	0.7	1.8	3.1	64

TABLE 4

EFFECT OF DI-ISOCYANATE ON PHYSICAL PROPERTIES OF UNAGED POLYURETHANE ELASTOMERS USING TMP CURE

Type of Di-isocyanate	Polyester (Ethylene Adipate)							Polyether (Polyoxybutylene Glycol)						
	Code S No	Tensile Strength, MN/m^2	Extension at Break, %	Modulus at (%)			Hardness, BS°	Code S No	Tensile Strength, MN/m^2	Extension at Break, %	Modulus at (%)			Hardness, BS°
				100	200	300					100	200	300	
_DI 80/20	111 A	24.9	350	1.9	3.2	7.4	71	119 A	2.9	180	1.5	-	-	76
NDI	112 B	16.0	400	0.4	1.3	2.8	67	121 B	3.0	120	1.3	-	-	74
MDI	113 B	20.9	420	0.8	2.2	12.8	69	122 B	4.2	250	0.6	2.0	-	67
HDI	114 B	26.1	485	3.8	4.0	8.1	96	-	-	-	-	-	-	-
MDI (mod)		-	-	-	-	-	-	124 B	3.9	245	0.8	-	-	82
MCI		-	-	-	-	-	-	125 B	0.7	280	0.1	0.6	-	39

TABLE 5

EFFECT OF TYPE OF TOLUENE DI-ISOCYANATE ISOMER USING TMP/MOCA CURE

Type of Di-isocyanate	Polyester (Ethyleno Adipate)							Polyether (Polyoxybutylene Glycol)						
	Code S No	Tensile Strength, MN/m	Extension at Break, %	Modulus at (%)			Hardness, BS°	Code S No	Tensile Strength, MN/m	Extension at Break, %	Modulus at (%)			Hardness, BS°
				100	200	300					100	200	300	
100% 2,4	110	48.7	515	1.9	3.2	6.2	85	118	8.9	235	4.4	7.8	-	90
80% 2,4 20% 2,6	110 A	36.0	545	2.4	3.1	6.4	85	119	16.9	345	3.0	5.3	9.9	89
65% 2,4 35% 2,6	111	30.2	490	2.4	3.9	7.2	88	120	10.5	225	3.5	5.6	-	89

cured solely with TMP. However, TMP cured polyester urethane elastomers, unlike TMP cured polyether elastomers, generally gave adequate mechanical properties.

The TMP/MOCA cured system gave harder elastomers with higher 100 per cent modulus values with both the polyester and polyether prepolymers.

The ultimate tensile strengths of the polyester urethanes were superior to those of the polyethers although their moduli and hardness were similar.

The tensile properties of the polyesters were generally good, although the TMP cured materials based on NDI and MDI and the TMP/MOCA cured material based on MCI were of lower hardness and lower modulus.

Of the polyethers only the TMP/MOCA cured materials based on TDI, HDI, XDI and IPDI had high ultimate tensile strengths although the IPDI material was rather soft. However, the MDI and NDI based elastomers had good hardness and modulus values, but possessed low extensions at break.

Table 5 compares the physical properties of TMP/MOCA cured polyester and polyether urethanes prepared from the three different TDI isomer mixtures available commercially. There appears to be a general advantage in using the 100% 2,4 isomer but the 80/20, 2,4/2,6 mixed isomers appear to be slightly superior to the 65/35 mixture.

4 3 2 Ageing in Dry Air (80°C)

After ageing in dry air for 28 days at 80°C, Tables 6 and 7 show that while the majority of polyester urethane elastomers show increases in 100 per cent modulus with small changes in hardness, the majority of the polyether urethanes show losses of both 100 per cent modulus and hardness. Other changes in mechanical properties appear to be more dependent on the type of di-isocyanate used rather than on the polyol backbone or method of chemical cure.

With the various TDI isomers the pattern is rather confused. The general trend however is for increases in 100% modulus and loss of hardness with polyester urethanes and for increased extensions at break, losses of 100% modulus and hardness in polyether urethanes.

TMP/MOCA cured polyester and polyether urethanes based on XDI showed considerable losses of tensile strength and extension at break as did TMP/MOCA cured polyether urethanes based on HDI, TMHDI and IPDI. Judged by retention of their original mechanical properties after ageing at 80°C the best elastomers were TMP/MOCA cured polyester urethanes based on TDI and MCI and TMP cured polyester urethanes based on TDI and MDI. TMP cured polyethers based on TDI and MDI (mod) were also quite satisfactory together with TMP/MOCA cured polyether urethanes based on TDI 80/20 and 65/35.

The apparent difficulty in interpreting the effects of heat ageing on polyurethane elastomers is according to Wright[3] due to firstly a temporary

TABLE 6

EFFECT OF AGEING IN DRY AIR AT 80°C ON PHYSICAL PROPERTIES OF POLYURETHANE ELASTOMERS PREPARED WITH DIFFERENT DI-ISOCYANATES

TMP/MOCA CURE

Type of Di-isocyanate	Code S No	Polyester (Ethylene Adipate) Percentage change of original mechanical properties				Code S No	Polyether (Polyoxybutylene Glycol) Percentage change of original mechanical properties			
		Tensile Strength	Extension at Break	Modulus at 100% Extension	Hardness		Tensile Strength	Extension at Break	Modulus at 100% Extension	Hardness
TDI 100	110	-32	0	+ 26	- 7	118	+67	+49	- 17	- 7
TDI 80/20	110 A	-34	+40	- 17	+14	119	+ 7	+20	- 13	- 2
TDI 65/35	111	+ 3	+ 3	+ 38	- 6	120	+ 2	+42	- 6	- 6
MCI	117 A	+22	0	+ 54	+15	125 A	+14	-16	+130	+15
XDI	132 A	-68	-21	+309	+ 1	133 A	-92	-19	- 46	- 7
NDI	-	-	-	-	-	121 A	+26	-29	-	-18
HDI	-	-	-	-	-	123 A	-76	- 8	- 50	-17
TMHDI	-	-	-	-	-	126 A	-79	-16	- 94	-44
IPDI	-	-	-	-	-	127 A	-65	0	- 86	-11

TABLE 7

EFFECT OF AGEING IN DRY AIR AT 80°C ON PHYSICAL PROPERTIES OF POLYURETHANE ELASTOMERS PREPARED WITH DIFFERENT DI-ISOCYANATES

TMP CURE

Type of Di-isocyanate	Code S No	Polyester (Ethylene Adipate)				Code S No	Polyether (Polyoxybutylene Glycol)			
		Percentage change of original mechanical properties					Percentage change of original mechanical properties			
		Tensile Strength	Extension at Break	Modulus at 100% Extension	Hardness		Tensile Strength	Extension at Break	Modulus at 100% Extension	Hardness
TDI 80/20	111 A	+30	- 3	+ 12	-3	119 A	-35	+14	-43	- 6.0
NDI	112 B	+46	- 3	+200	-1	121 B	+23	+50	+46	0
MDI	113 B	-15	- 4	0	-7	122 B	-52	- 2	0	-10
HDI	114 B	-67	-29	+ 32	+8	-	-	-	-	-
MDI mod	-	-	-	-	-	124 B	-15	-23	-	-20

fall off in properties due to a general weakening of the physical bonds within the polymer. The second process which occurs is a non-reversible destructive change in the chemical structure and there is little evidence of this occurring below temperatures of 70°C. Not only do some elastomers show a recovery of original properties after removal from the source of heat but others show an improvement in certain physical properties which may be due to the formation of allophanate and/or biuret crosslinks. Deterioration of properties is probably due to the fact that secondary chemical bonds are more easily broken than primary bonds especially at elevated temperatures.

Athey[9] has shown with a MOCA cure polyoxybutylene glycol urethane that after 15 days at 70°C there was an increase of 100 per cent modulus and tensile strength but a decrease after longer periods of heating. Extension at break increased with time while tear strength decreased. On the other hand, at 100°C while tensile strength and 100 per cent modulus decreased tear strength and extension at break increased.

Polyether urethanes are probably inherently less stable to higher temperatures than polyester urethanes due to oxidative cleavage of the ether linkage.

This has been confirmed experimentally by Singh[10] using continuous and intermittent stress relaxation and oven ageing studies at 50 - 150°C using polyethylene adipate and polyoxybutylene glycol/2,4 TDI prepolymers crosslinked with TMP.

The general concensus of opinion is that the maximum continuous working temperature for conventional polyurethane elastomers is 70 - 80°C.

4 3 3 Water Immersion (22°C)

After 28 days' immersion in water at 22°C (Table 8) there were few differences between the changes in original mechanical properties of TMP/MOCA cured polyester and polyether urethanes based on TDI 100 and TDI 65/35. Polyester urethane based on XDI was not greatly changed, but the polyether based on the same di-isocyanate suffered severe stress cracking. Even under these mild conditions some of the elastomers showed considerable changes in properties particularly the polyester based on NDI, the TMP/MOCA cured polyethers based on IPDI and the TMP cured polyether based on MDI (mod).

Elastomers showing the best retention of original properties were TMP/MOCA cured polyether urethanes based on HDI and TDI 100; TMP/MOCA cured polyester urethanes based on MCI and XDI and TMP cured polyester urethane based on MDI.

4 3 4 Water Immersion (80°C)

The effects of 28 days' immersion in water at 80°C on urethane elastomers also shown in Tables 8 and 9 are more significant than the effects described above. All the polyester urethanes were severely degraded;

TABLE 8

EFFECT OF IMMERSION IN WATER AT 22 AND 80°C ON PHYSICAL PROPERTIES OF POLYURETHANE ELASTOMERS PREPARED WITH DIFFERENT DI-ISOCYANATES

TMP/MOCA CURE

Type of Di-isocyanate	28 days' Immersion in Water at (°C)	Code S No	Polyester (Ethylene Adipate) Percentage change of original mechanical properties: Tensile Strength	Extension at Break	Modulus at 100% Extension	Hardness	Code S No	Polyether (Polyoxybutylene Glycol) Percentage change of original mechanical properties: Tensile Strength	Extension at Break	Modulus at 100% Extension	Hardness
TDI 100	22	110	-26	-3	0	- 8	118	-17	+ 2	- 20	- 1
	80	110	Too weak to test				118	-33	+ 60	- 61	-16
TDI 80/20	22	110 A	-23	-4	0	- 6	-	-	-	-	-
	80	110 A	Too weak to test				119	+34	+ 72	- 19	- 3
TDI 65/35	22	111	-24	-5	0	- 7	120	-23	+ 20	- 9	- 2
	80	111	Too weak to test				120	- 6	+122	- 46	-18
MCI	22	117 A	-16	-8	+38	+ 1	-	-	-	-	-
	80	117 A	Disintegrated				125 A	-38	+ 16	- 20	-17
XDI	22	132 A	- 2	+5	+45	-12	133 A	-50	- 10	+ 31	-61
	80	132 A	Too weak to test				133 A	-70	- 6	- 54	-63
HDI	22						123 A	- 2	+ 1	- 13	- 3
	80						123 A	-51	+ 26	- 13	-46
TMHDI	22						126 A	-25	+ 1	+133	- 5
	80						126 A	-77	+ 13	- 94	-28
IPDI	22						127 A	-47	- 15	+ 86	0
	80						127 A	-65	+ 21	- 71	-36

TABLE 9

EFFECT OF IMMERSION IN WATER AT 22 AND 80°C ON PHYSICAL PROPERTIES OF POLYURETHANE ELASTOMERS PREPARED WITH DIFFERENT DI-ISOCYANATES

TMP CURE

Type of Di-isocyanate	28 days' Immersion in Water at (°C)	Code S No	Polyester (Ethylene Adipate)				Code S No	Polyether (Polyoxybutylene Glycol)			
			Percentage change of original mechanical properties					Percentage change of original mechanical properties			
			Tensile Strength	Extension at Break	Modulus at 100% Extension	Hardness		Tensile Strength	Extension at Break	Modulus at 100% Extension	Hardness
TDI 80/20	22	111 A	-	-	-	-	119 A	-	-	-	-
	80	111 A	Disintegrated				119 A	- 39	+195	- 77	-10
NDI	20	112 B	+42	+5	+175	-3	121 B	- 27	+ 17	- 15	0
	80	112 B	Disintegrated				121 B	+ 90	+146	- 46	-20
MDI	20	113 B	- 1	+4	- 4	-4	122 B	- 55	- 24	+ 50	- 1
	80	113 B	Disintegrated				122 B	- 7	+ 42	- 33	-21
HDI	20	114 B	-18	-7	- 37	-8		-	-	-	-
	80	114 B	Disintegrated					-	-	-	-
MDI (mod)	20	-	-	-	-	-	124 B	- 72	- 47	+ 25	-21
	80	-	-	..	-	-	124 B	+ 8	+ 78	- 75	-35
MCI	20	-	-	-	-	-	125 B	-	-	-	-
	80	-	-	-	-	-	125 B	+185	+ 79	+100	-28

TABLE 10

EFFECT OF IMMERSION IN PETROL (STF) AT 65°C ON PHYSICAL PROPERTIES OF POLYURETHANE ELASTOMERS PREPARED WITH DIFFERENT DI-ISOCYANATES

TMP/MOCA CURE

Type of Di-isocyanate	Code S No	Polyester (Ethylene Adipate)				Code S No	Polyether (Polyoxybutylene Glycol)			
		Percentage change of original mechanical properties					Percentage change of original mechanical properties			
		Tensile Strength	Extension at Break	Modulus at 100% Extension	Hardness		Tensile Strength	Extension at Break	Modulus at 100% Extension	Hardness
TDI 100	110	-31	- 1	+21	-11	118	-43	-51	+16	-13
TDI 80/20	110 A	-31	- 5	+20	-10	119	-52	-56	-	- 8
TDI 65/35	111	-32	- 9	+25	-10	120	-58	-56	+26	-15
MCI	117 A	-45	-27	-54	-24	125 A	-62	-40	-30	-14
XDI	132 A	-22	+ 8	-18	- 9	133 A	-88	-50	-38	-70
HDI	-	-	-	-	-	123 A	-57	-10	-75	-60
TMHDI	-	-	-	-	-	126 A	-80	-38	-67	-50
IDI	-	-	-	-	-	127 A	-82	-45	-43	-47

TABLE 11

EFFECT OF IMMERSION IN PETROL (STF) AT 65°C ON PHYSICAL PROPERTIES OF POLYURETHANE ELASTOMERS PREPARED WITH DIFFERENT DI-ISOCYANATES

TMP CURE

Type of Di-isocyanate	Code S No	Polyester (Ethylene Adipate)				Code S No	Polyether (Polyoxybutylene Glycol)			
		Percentage change of original mechanical properties					Percentage change of original mechanical properties			
		Tensile Strength	Extension at Break	Modulus at 100% Extension	Hardness		Tensile Strength	Extension at Break	Modulus at 100% Extension	Hardness
TDI 80/20	111 A	-84	-29	- 53	- 1	119 A	-77	-50	-17	-18
NDI	112 B	-48	-15	+100	- 6	121 B	-70	-54	-	- 9
MDI	113 B	-78	-21	- 13	-16	122 B	-83	-64	-	-25
HDI	114 B	-55	- 5	- 8	-36	-	-	-	-	-
MDI mod	-	-	-	-	-	124 B	-87	-47	-50	-51

TMP/MOCA cured polyester elastomers based on TDI and XDI were intact but too weak to test, while the remainder based on TMP/MOCA cured MCI, XDI and TMP cured NDI, MDI and HDI polyester elastomers disintegrated.

TMP/MOCA cured polyether urethanes based on TDI 100, TDI 80/20, TDI 65/35 and MCI showed reasonable retention of properties. TMP cured polyether urethanes based on TDI 80/20, NDI, MDI and MDI (mod) were also fairly satisfactory but rather soft.

TMP/MOCA cured polyether urethanes based on XDI, HDI, TMHDI and IPDI showed large changes in properties.

4 3 5 Immersion in Petrol (STF) (65°C)

Tables 10 and 11 show that after 28 days' immersion in STF at 65°C polyester urethane elastomers, especially when cured with TMP/MOCA, are less susceptible to attack than polyether urethane elastomers prepared with the same di-isocyanates. Similarly, TMP/MOCA cured polyether urethanes prepared with TDI 80 and HDI were better than TMP cured polyether urethanes based on the same di-isocyanates.

The elastomers showing the best retention of original mechanical properties were TMP/MOCA cured polyester urethanes based on TDI and XDI.

None of the polyether urethanes, apart from TMP/MOCA cured TDI 100 and 80/20 elastomers had satisfactory resistance to STF at 65°C.

5 DISCUSSION

Toluene di-isocyanate (which is chemically one aromatic ring group with a methyl substituent) was the most versatile of all the di-isocyanates examined; all three isomeric forms of this isocyanate produced easily processed polyether or polyester prepolymers capable of being cured with either 1,1',1"-trimethylol propane (TMP) or trimethylol propane/methyl bis-(2-chloroaniline) (MOCA) mixtures. TMP/MOCA cured TDI/polyester urethane elastomers especially, gave good initial physical properties together with satisfactory resistance to dry air at 80°C, water at 22°C and petrol (STF) at 65°C; but their resistance to water at 80°C was extremely poor. On the other hand, similarly cured polyether/TDI prepolymers produced polyurethane elastomers with satisfactory initial physical properties coupled with satisfactory resistance to dry air at 80°C, water at 22 and 80°C, but with only fair resistance to STF at 65°C. A further advantage of TDI is that it is a readily available liquid of relatively low cost (about 3s 6d per lb (17.5p)) but having the disadvantages of a high vapour pressure, unpleasant odour and possible toxicity. Adequate precautions and good ventilation are necessary for its use.

None of the other di-isocyanates examined produced elastomers with the all round properties equal to those based on TDI although 1,5-naphthalene di-isocyanate (NDI) and 4,4-diphenyl methane di-isocyanate (MDI), which chemically are large rigid symmetrical structures containing two aromatic

rings, and HDI, an aliphatic di-isocyanate, had the advantage of producing TMP cured polyester urethanes with fairly good all round mechanical properties. NDI and MDI also produced TMP cured polyether urethanes with fairly satisfactory resistance to dry air and water at 22 and 80°C. A disadvantage of both these di-isocyanates is their very high reactivities to MOCA or similar amines and that they produce elastomers which are coloured, especially after ageing. Their high cost (MDI 6s 0d per lb (30p), NDI £1 per lb (100p)) and limited availability at present are further disadvantages. Although MDI is a solid of low vapour pressure it has a tendency to unstable due to dimerization on storage. A modified MDI in liquid form was also examined but did not appear to offer any other specific advantages over MDI in polyester or polyether urethanes.

A number of promising TMP/MOCA polyester urethanes were prepared using 4,4'-methylene bis-cyclohexyl di-isocyanate, MCI, a liquid cycloaliphatic di-isocyanate which produced elastomers with good resistance to dry air at 80°C, water (at 22°C only) and STF at 65°C. Particularly disappointing were the performances of liquid di-isocyanates, viz trimethylhexamethylene di-isocyanate, TMHDI, an aliphatic di-isocyanate and isophorone di-isocyanate, IPDI, an aliphatic-cycloaliphatic di-isocyanate, which generally produced soft slow curing elastomers. The main advantage of this type of di-isocyanate, together with HDI, may be in their non-yellowing properties of elastomers exposed to sources of photo-oxidative degradation. A further liquid di-isocyanate, a mixture of 70 per cent meta- and 30 per cent para-xylene di-isocyanates (XDI) which chemically comprises an aromatic group with an aralkyl substituent and is available in sample quantities from Japan, and which, while proving to be reasonably effective in polyester urethanes, yielded polyether urethanes which showed severe stress cracking on ageing in water at 22 and 80°C, and STF at 65°C.

Two other di-isocyanates which were also of interest but arrived too late for evaluation in the present investigation were O-toluidine di-isocyanate (TODI)[11] and dianisidine di-isocyanate (DADI), both of which would be expected to behave in a similar manner to NDI and MDI. In addition, a high molecular weight dimer acid derived di-isocyanate (DDI) is at present being examined in conjunction with a TMP/MOCA cured laboratory prepared low molecular weight butadiene/butyraldehyde copolymer.

Summarising the results of the present investigation in conjunction with those of earlier investigations,[1-4] these confirm that polyurethane elastomers with satisfactory resistance to ageing (for the purpose of this report losses of not more than one-third their initial tensile strengths, extensions at break, 100 per cent moduli and hardnesses after 28 days' exposure to selected environments are considered the criteria of satisfactory resistance to ageing) may be prepared from MOCA or TMP/MOCA cured polyester, polyether or hydroxyl-terminated polybutadiene/toluene di-isocyanate prepolymers; few systems however have been found which satisfy these oriterea for all three chosen environments namely hot wet, hot dry and STF.

For example, urethanes prepared with polyethylene adipate or polyethylene/propylene adipates have produced elastomers with good initial physical

properties, for example, tensile strengths of 40 - 50 MN/m^2 (6000 - 7000 lb/in), extension at break of 400 - 600 per cent, 100 per cent moduli of 2.5 - 4.0 MN/m and hardness values of 80 - 90 BS°. Polyester urethane elastomers have been formulated which show satisfactory ageing properties after ageing in dry air at 80°C, immersion in water at 22°C and petrol at 65°C but no elastomers based on adipate esters have been found to be capable of withstanding water immersion at 80°C. This has confirmed our belief that the ester group in these urethanes is responsible for the poor hydrolytic stability at elevated temperatures. This instability is almost independent of changes in chemical structure, although marginal improvements appear to be achieved by the introduction of biuret crosslinks and aromatic, eg urea groups, which may offer some protection to the ester groups.

The best polyether urethanes produce elastomers which usually have initial properties rather inferior to polyester urethanes, for example ultimate tensile strengths of 20 - 35 MN/m^2 (3000 - 5000 lb/in^2) with extensions at break of 350 - 450 per cent; but with 100 per cent moduli of 5 - 6 MN/m^2 and hardness values of 90 - 99 BS°, ie similar or rather better than those of polyester urethanes. Polyether urethane elastomers have been shown to give satisfactory resistance to dry air at 80°C and are only slightly inferior to polyester urethanes in this respect and fairly good hydrolytic stability at 22 and 80°C. Polyether urethanes while showing moderate resistance to petrol at 65°C, judged by retention of original properties on recovery, were usually swollen while actually immersed in the petrol. Improved resistance to swelling by petrol is achieved, to some extent, by increasing the degree of crosslinking of the elastomer.

Hydroxyl-terminated polybutadiene/TDI prepolymers crosslinked with diols gave urethane elastomers with inferior initial physical properties compared to those based on polyesters and polyethers, having tensile strengths of 7.0 - 11.0 MN/m^2 (1000 - 1500 lb/in^2), extensions at break of 200 - 300 per cent, with 100 per cent moduli of 3.0 - 5.0 MN/m and hardness values of 70 - 85 BS°. The hydrolytic stability of these elastomers at 80°C is outstanding and their resistance to dry air at 80°C is satisfactory; unfortunately the resistance of these elastomers to petrol at 65°C was rather poor.

6 CONCLUSIONS

The results of the present investigation shows that of the di-isocyanates available for use in polyurethanes, elastomers prepared with toluene di-isocyanate show the best all round properties, judged by initial mechanical properties and retention of original properties after ageing in dry air, water and STF (petrol).

For applications where the use of MOCA is restricted, 1,6-hexamethylene di-isocyanate, 4,4-diphenyl methane di-isocyanate and 1,6-naphthalene di-isocyanate are capable of producing satisfactory urethane elastomers when cured with triols.

These results, in conjunction with those of earlier investigations in the present series[1-4] show that polyurethane elastomers with good ageing properties in selected environments may be prepared with polyester or polyether or hydroxyl-terminated polybutadiene/toluene di-isocyanate prepolymers preferably containing an excess of isocyanate, of average molecular weight 2000 - 2500. The polyester and polyether prepolymers are preferably chain extended or crosslinked with MOCA or TMP/MOCA mixtures in less than stoichiometric equivalents to the di-isocyanate, so as to introduce both aromatic urea groups and a moderate degree of biuret crosslinking.

No polyester urethane has been found to be capable of withstanding water at 80°C.

The only polyurethanes to show reasonable retention of properties to all the environments were polyether TDI prepolymers crosslinked with TMP/MOCA giving a calculated molecular weight between crosslinks of less than 2000 or alternatively polyethers chain extended with TDI and crosslinked with less than stoichiometric amounts of MOCA again to give $M_c < 2000$.

7 FURTHER WORK

Certain further investigations into the ageing properties of polyurethane elastomers are in progress, including the assessment of commercially supplied ε-caprolactone polyesters, and hydroxyl-terminated polybutadiene elastomers prepared using more rigid aromatic di-isocyanates and chain extenders. The influence of various additives on the ageing properties of polyurethanes are also being assessed by natural and accelerated weathering trials; the results of these studies will be reported in due course.

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METHODS OF PREPARATION

PREPOLYMERS

All the elastomers were prepared via prepolymers as follows.

The selected di-isocyanate, 2.1 mole equivalent, was placed into a dried 500 ml glass three-necked flask equipped with thermometer stirrer, nitrogen and vacuum-inlet and heated to 80°C under nitrogen. Melted polyol, 1.0 mole equivalent, previously degassed by heating to 120 - 125°C for 30 minutes and applying a vacuum of 1 mmHg, was added to the di-isocyanate over a period of 30 minutes. The mixture was heated under nitrogen with continuous stirring at temperatures which varied from 3 hours at 80 - 85°C for toluene di-isocyanate to 1½ hours at 130°C for naphthalene di-isocyanate; during the last 30 minutes a vacuum of 1mmHg was applied.

The di-isocyanate prepolymer was transferred to a dried 600 ml beaker and degassed under 1 mmHg vacuum for 10 minutes. Crosslinking or chain extending agents: TMP 0.66 mole equivalent, equal parts of TMP/MOCA* (TMP 0.33 mole equivalent and MOCA 0.50 mole equivalent) (Table 2), were stirred into the prepolymer. The mixture was reheated 60 - 80°C and degassed for 1 - 15 minutes at 1 mmHg.

The reaction products were poured into PTFE coated aluminium trays and cured in an oven for 16 hours at 90°C to produce sheets 220 x 150 mm approximately 25 mm thick.

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*Reports[10] on the hazards in the use of MOCA are somewhat conflicting. Briefly MOCA shows the general toxicity characteristics of the halogenated aromatic amines, and when taken into the body may produce cyanosis; although it may cause dermatitis on animals there is no direct evidence of it causing it on humans. On thermal breakdown it gives off an irritating gaseous product. MOCA produces liver cancer when given to rats fed on a protein deficient diet. Recent tests for its carcinogenacity using dogs fed 100 mg per day for 14 months gave no bladder tumours. However tests will continue for 4 - 5 years and great caution in its use is advised.

TABLE 12

GENERAL CONDITION AND APPEARANCE OF POLYURETHANE ELASTOMERS PREPARED WITH DIFFERENT DI-ISOCYANATES SELECTED FOR ASSESSMENT OF AGEING PROPERTIES

Code Number	Polyol	Di-isocyanate	Cross Linker/ Chain Extender	Unaged Controls	Dry Air 28 days at 80°C
S 110	Polyester (Ethylene adipate)	Toluene 100% 2,4-	TMP/MOCA	clear transparent, very tough	very slightly more yellow, tough
S 110A		Toluene 80% 2,4- 20% 2,6-	TMP/MOCA	clear transparent, tough	slightly more yellow, tough
S 111		Toluene 65% 2,4- 35% 2,6-	TMP/MOCA	very pale yellow, slightly translucent, tough	more yellow, tough
S 111A		Toluene 65% 2,4- 35% 2,6-	TMP	very pale yellow, slightly translucent, flexible	more yellow, flexible
S 112B		1,5-Naphthalene	TMP	very pale brown, fairly tough - flexible	more brown, very tough
S 113B		4,4-Diphenyl methane	TMP	pale brown, tough, rigid	slightly more brown, tough
S 114B		1,6-Hexamethylene	TMP	white opaque, tough	little change, less tough
S 117A		Methylene bis-cyclohexyl	TMP/MOCA	very pale yellow, tough	slightly more yellow, very tough
S 132A		Xylene	TMP/MOCA	very pale yellow, translucent, tough	slightly more yellow, wetter
S 118	Polyether (Polyoxybutylene glycol)	Toluene 100% 2,4-	TMP/MOCA	very pale yellow, translucent, fairly tough	more yellow, tough

H

ols	Dry Air 28 days at 80°C	Water immersion 28 days at		STF (Petrol) 28 days at 65°C	
		22°C	80°C	Degree of Swelling	
				On Removal	On Recovery
rent,	very slightly more yellow, tough	little change	intact but severe discoloration and loss of strength	slight	little change of colour, slight loss of strength
rent,	slightly more yellow, tough	little change	intact but severe discoloration and loss of strength	very slight-slight	little change of colour, slight loss of strength
llow, slu-	more yellow, tough	little change, slightly less yellow	intact but severe discoloration and loss of strength	very slight-slight	little change of colour, slight loss of strength
llow, slu- e	more yellow, flexible	little change, slightly less yellow	catastrophic failure, brown viscous liquid	slight	little change of colour, slight loss of strength
wn,	more brown, very tough	slightly more amber, strength unchanged	catastrophic failure, black viscous liquid	very slight	deep amber, moderate loss of strength
ough,	slightly more brown, tough	little change	catastrophic failure, brown viscous liquid	slight	rather more amber, moderate loss of strength
	little change, less tough	little change	catastrophic failure, yellow viscous liquid	slight	little change, moderate loss of strength
low,	slightly more yellow, very tough	little change	severe discoloration, opaque mass, no strength	slight	little change of colour, moderate loss of strength
llow,	slightly more yellow, wetter	little change	intact but moderate discoloration and considerable loss of strength	moderate	little change of colour, slight loss of strength
llow,	more yellow, tough	slightly more yellow, no change in strength	amber, fairly tough	slight-moderate	little change of colour, moderate [illegible] strength

TABLE 12 (Contd)

Code Number	Polyol	Di-isocyanate	Cross Linker/ Chain Extender	Unaged Controls	Dry Air 28 days at 80°C
S 119	**Polyether (Polyoxybutylene glycol)**	Toluene 80% 2,4- 20% 2,6-	TMP/MOCA	clear transparent, moderately tough	slightly more yellow, fairly tough
S 120		Toluene 65% 2,4- 35% 2,6-	TMP/MOCA	very pale yellow, fair - moderately tough	more yellow, tough
S 121B		1,5-Naphthalene	TMP	brown, flexible	considerably more brown, tough
S 122B		4,4-Diphenyl methane	TMP	clear wrinkled, very flexible	more yellow, less tough
S 123A		1,6-Hexamethylene	TMP/MOCA	very pale yellow, tough	slightly more yellow, less tough
S 124B		Modified 4,4-diphenyl methane	TMP	clear transparent, rather weak	slightly more yellow, little change of strength
S 125A		Methylene bis-cyclohexyl	TMP/MOCA	very pale yellow, rather weak	little change of colour or strength
S 126A		Trimethylhexa-methylene	TMP/MOCA	very pale yellow, translucent, fairly tough and elastic	slightly more yellow, less tough
S 127A		Isophorone	TMP/MOCA	very pale yellow, tough	slightly more yellow, less tough
S 133A		Xylene	TMP/MOCA	pale yellow opaque, tough	considerably more yellow and less tough, severe stress cracking

ontrols	Dry Air 28 days at 80°C	Water immersion 28 days at 22°C	80°C	STF (Petrol) 28 days at 65°C Degree of Swelling On Removal	On Recovery
sparent, tough	slightly more yellow, fairly tough	slightly more yellow, no change in strength	amber, fairly tough	slight-moderate	little change of colour, moderate loss of strength
yellow, erately	more yellow, tough	slightly more yellow, no change in strength	amber, fairly tough	slight-moderate	little change of colour, moderate loss of strength
xible	considerably more brown, tough	little change	dark brown, fairly tough	slight	more amber, considerable loss of strength
kled, ble	more yellow, less tough	little change	slightly more yellow, little loss of strength	slight-moderate	slightly more yellow, considerable loss of strength
ellow,	slightly more yellow, less tough	little change	little change in colour, some loss of strength	moderate	little change of colour, moderate loss of strength
parent,	slightly more yellow, little change of strength	little change	very slightly more brown, little change of strength	slight-moderate	very slightly more yellow, considerable loss of strength
ellow,	little change of colour or strength	little change	very slightly more brown, little change of strength	moderate	little change of colour, moderate loss of strength
ellow, , h and	slightly more yellow, less tough	little change	little change of colour, rather weak	severe	little change of colour, considerable loss of strength
yellow,	slightly more yellow, less tough	little change	little change of colour, some loss of strength	moderate-severe	little change of colour, considerable loss of strength, more orange
gh	considerably more yellow and less tough, severe stress cracking	less opaque, severe stress cracking	less opaque, severe stress cracking	severe	considerable loss of strength

TABLE 13

MECHANICAL PROPERTIES OF POLYURETHANE ELASTOMERS PREPARED
WITH DIFFERENT DI-ISOCYANATES BEFORE AND AFTER AGEING

Key:
- TS — Tensile strength
- EB — Extension at break
- M_{100}, M_{200}, M_{300} — Moduli at extensions of 100, 200 and 300 per cent
- H — Hardness
- \- — Value not recorded or too low to be accurately recorded

Code Number	Polyol	Di-isocyanate	Cross Linker/ Chain Extender	Original Properties (Unaged Controls)						
				TS MN/m^2	EB %	M_{100} MN/m^2	M_{200} MN/m^2	M_{300} MN/m^2	H BS^o	TS MN/m^2
S 110	Polyester (Ethylene adipate)	TDI 100	TMP/MOCA	48.7	515	1.9	3.2	6.2	85	32.9
S 110A		TDI 80/20	TMP/MOCA	36.0	545	2.4	3.1	6.4	85	23.8
S 111		TDI 65/35	TMP/MOCA	30.2	490	2.4	3.9	7.2	88	31.2
S 111A		TDI 80/20	TMP	24.9	350	1.9	3.2	7.4	71	32.6
S 112A		NDI	TMP/MOCA	18.1	390	3.4	6.0	13.1	91	-
S 112B		NDI	TMP	16.0	400	0.4	1.3	2.8	67	23.4
S 113A		MDI	TMP/MOCA	22.7	420	2.6	5.0	10.0	89	-
S 113B		MDI	TMP	20.9	420	0.8	2.2	12.8	69	17.7
S 114A		HDI	TMP/MOCA	17.9	490	5.4	5.4	7.1	99	-
S 114B		HDI	TMP	26.1	485	3.8	4.0	8.1	96	8.6
S 116A		MDI mod	TMP/MOCA	26.2	355	3.8	6.7	16.7	89	-
S 117A		MCI	TMP/MOCA	33.2	550	1.3	2.8	6.0	67	40.6
S 132A		XDI	TMP/MOCA	30.5	550	2.2	3.3	5.5	97	9.7
S 132B		XDI	TMP	16.6	430	2.2	3.8	9.6	83	-

ent

recorded

Note: $6.9 \text{ MN/m}^2 = 1000 \text{ lb/in}^2$

Properties Controls)			28 Days in Dry Air at 80°C						28 Days Immersion in Water at 22°C					
M_{200} MN/m²	M_{300} MN/m²	H BS°	TS MN/m²	EB %	M_{100} MN/m²	M_{200} MN/m²	M_{300} MN/m²	H BS°	TS MN/m²	EB %	M_{100} MN/m²	M_{200} MN/m²	M_{300} MN/m²	H BS°
3.2	6.2	85	32.9	515	2.4	3.5	5.8	79	35.6	500	1.9	3.1	5.3	78
3.1	6.4	85	23.8	765	2.0	2.7	3.9	97	27.7	620	2.4	3.25	5.1	80
3.9	7.2	88	31.2	505	3.3	5.4	8.6	83	23.0	465	2.4	4.3	7.0	82
3.2	7.4	71	32.6	340	2.0	2.3	4.9	69	-	-	-	-	-	-
6.0	13.1	91	-	-	-	-	-	-	22.7	420	1.1	2.2	3.8	65
1.3	2.8	67	23.4	390	1.2	2.5	4.9	66	-	-	-	-	-	-
5.0	10.0	89	-	-	-	-	-	-	-	-	-	-	-	-
2.2	12.8	69	17.7	405	0.8	1.8	3.1	64	20.7	435	0.7	1.5	3.2	66
5.4	7.1	99	-	-	-	-	-	-	-	-	-	-	-	-
4.0	8.1	96	8.6	345	5.0	5.1	6.8	98	21.3	450	2.4	3.2	6.3	88
6.7	16.7	89	-	-	-	-	-	-	-	-	-	-	-	-
2.8	6.0	67	40.6	550	2.0	3.7	7.0	77	27.8	505	1.8	3.0	5.2	68
3.3	5.5	97	9.7	435	9.0	9.1	9.1	98	30.0	575	3.2	3.9	5.7	85
3.8	9.6	83	-	-	-	-	-	-	-	-	-	-	-	-

TABLE 13 (Contd)

MECHANICAL PROPERTIES OF POLYURETHANE ELASTOMERS PREPARED WITH DIFFERENT DI-ISOCYANATES BEFORE AND AFTER AGEING

Key:	
TS	Tensile strength
EB	Extension at break
M_{100}, M_{200}, M_{300}	Moduli at extensions of 100, 200 and 300 per cent
H	Hardness
-	Value not recorded or too low to be accurately recorded

Code Number	Polyol	Di-isocyanate	Cross Linker/ Chain Extender	Original Properties (Unaged Controls)						
				TS MN/m^2	EB %	M_{100} MN/m^2	M_{200} MN/m^2	M_{300} MN/m^2	H BS^{o}	TS MN/m^2
S 118	Polyether (Polyoxybutylene glycol)	TDI 100	TMP/MOCA	8.9	235	4.4	7.8	-	90	14.9
S 119		TDI 80/20	TMP/MOCA	16.9	345	3.0	5.3	9.9	89	17.8
S 120		TDI 65/35	TMP/MOCA	10.5	225	3.5	5.6	-	89	10.7
S 119A		TDI 80/20	TMP	2.9	180	1.5	-	-	76	3.1
S 121A		NDI	TMP/MOCA	3.9	120	3.5	-	-	90	4.9
S 121B		NDI	TMP	3.0	120	1.3	-	-	74	3.7
S 122A		MDI	TMP/MOCA	6.1	215	3.8	6.0	-	90	-
S 122B		MDI	TMP	4.2	250	0.6	2.0	-	67	2.0
S 123A		HDI	TMP/MOCA	13.6	460	0.8	0.8	1.6	65	3.3
S 124B		MDI mod	TMP	3.[illegible]	245	0.8	-	-	82	-
S 125A		MCI	TMP/MOCA	5.0	285	1.0	4.5	-	66	3.3
S 125B		MCI	TMP	0.7	280	0.1	0.6	-	39	-
S 126A		TMHDI	TMP/MOCA	5.6	430	0.3	0.8	1.5	57	1.2
S 127A		IDI	TMP/MOCA	15.9	445	0.7	1.8	3.1	64	5.5
S 133A		XDI	TMP/MOCA	18.8	565	1.3	1.9	3.1	82	1.6

ent

recorded

Note: 6.9 MN/m^2 = 1000 lb/in^2

l Properties d Controls)				28 Days in Dry Air at 80°C						28 Days Immersion in Water at 22°C					
o	M_{200}	M_{300}	H	TS	EB	M_{100}	M_{200}	M_{300}	H	TS	EB	M_{100}	M_{200}	M_{300}	H
$/m^2$	MN/m^2	MN/m^2	BS°	MN/m^2	%	MN/m^2	MN/m^2	MN/m^2	BS°	MN/m^2	%	MN/m^2	MN/m^2	MN/m^2	BS°
4	7.8	-	90	14.9	350	3.8	5.9	11.2	88	7.4	240	3.5	6.4	-	89
0	5.3	9.9	89	17.8	440	2.1	5.1	6.5	73	-	-	-	-	-	-
5	5.6	-	89	10.7	320	3.3	5.6	-	85	8.1	270	3.2	5.6	-	87
5	-	-	76	3.1	215	1.3	2.8	-	72	-	-	-	-	-	-
5	-	-	90	4.9	85	-	-	-	74	-	-	-	-	-	-
3	-	-	74	3.7	180	-	1.9	-	74	2.2	140	1.1	-	-	74
8	6.0	-	90	-	-	-	-	-	-	-	-	-	-	-	-
6	2.0	-	67	2.0	245	0.6	1.3	-	60	1.9	190	0.9	-	-	66
8	0.8	1.6	65	3.3	425	0.4	0.7	1.3	54	10.9	465	0.7	1.2	1.9	63
8	-	-	82	-	-	-	-	-	-	1.1	130	1.0	-	-	65
.0	4.5	-	66	3.3	200	-	-	-	66	4.4	240	1.9	2.8	-	69
1	0.6	-	39	-	-	-	-	-	-	-	-	-	-	-	-
3	0.8	1.5	57	1.2	360	-	0.2	0.6	32	4.2	485	-	-	0.2	41
7	1.8	3.1	64	5.5	445	0.1	0.8	1.8	57	8.5	380	1.3	2.1	3.7	64
3	1.9	3.1	82	1.6	460	0.7	0.8	1.0	76	9.3	510	1.7	2.2	3.1	32

TABLE 13 (Contd)

MECHANICAL PROPERTIES OF POLYURETHANE ELASTOMERS PREPARED WITH DIFFERENT DI-ISOCYANATES BEFORE AND AFTER AGEING

Key:

TS	Tensile strength
EB	Extension at break
M_{100}, M_{200}, M_{300}	Moduli at extensions of 100, 200 and 300 per cent
H	Hardness
-	Value not recorded or too low to be accurately recorded

Code Number	Polyol	Di-isocyanate	Cross Linker/ Chain Extender	Original Properties (Unaged Controls)						28
				TS MN/m^2	EB %	M_{100} MN/m^2	M_{200} MN/m^2	M_{300} MN/m^2	H BS°	TS MN/m^2
S 110	Polyester (Ethylene adipate)	TDI 100	TMP/MOCA	48.7	515	1.9	3.2	6.2	85	
S 110A		TDI 80/20	TMP/MOCA	36.0	545	2.4	3.1	6.4	85	
S 111		TDI 65/35	TMP/MOCA	30.2	490	2.4	3.9	7.2	88	
S 111A		TDI 80/20	TMP	24.9	350	1.9	3.2	7.4	71	
S 112A		NDI	TMP/MOCA	18.1	390	3.4	6.0	13.1	91	
S 112B		NDI	TMP	16.0	400	0.4	1.3	2.8	67	
S 113A		MDI	TMP/MOCA	22.7	420	2.6	5.0	10.0	89	
S 113B		MDI	TMP	20.9	420	0.8	2.2	12.8	69	
S 114A		HDI	TMP/MOCA	17.9	490	5.4	5.4	7.1	99	
S 114B		HDI	TMP	26.1	485	3.8	4.0	8.1	96	
S 116A		MDI mod	TMP/MOCA	26.2	355	3.8	6.7	16.7	89	
S 117A		MCI	TMP/MOCA	33.2	550	1.3	2.8	6.0	67	
S 132A		XDI	TMP/MOCA	30.5	550	2.2	3.3	5.5	97	
S 132B		XDI	TMP	16.6	430	2.2	3.8	9.6	83	

0 per cent

urately recorded

Note: $6.9 \text{ MN/m}^2 = 1000 \text{ lb/in}^2$

Original Properties (Unaged Controls)					28 Days Immersion in Water at 80°C						28 Days Immersion in STF at 65°C					
B %	M_{100} MN/m²	M_{200} MN/m²	M_{300} MN/m²	H BS°	TS MN/m²	EB %	M_{100} MN/m²	M_{200} MN/m²	M_{300} MN/m²	H BS°	TS MN/m²	EB %	M_{100} MN/m²	M_{200} MN/m²	M_{300} MN/m²	H BS°
15	1.9	3.2	6.2	85	Too weak to test						33.7	510	2.3	3.6	6.0	76
45	2.4	3.1	6.4	85	Too weak to test						24.9	518	1.9	3.5	7.0	77
0	2.4	3.9	7.2	88	Too weak to test						20.5	445	3.0	4.4	7.2	79
0	1.9	3.2	7.4	71	Disintegrated						4.1	250	0.9	2.7	-	70
0	3.4	6.0	13.1	91	Disintegrated						-	-	-	-	-	-
0	0.4	1.3	2.8	67	Disintegrated						8.3	355	0.8	2.2	4.1	63
0	2.6	5.0	10.0	89	Disintegrated						-	-	-	-	-	-
0	0.8	2.2	12.8	69	Disintegrated						4.7	330	0.7	1.7	3.2	58
0	5.4	5.4	7.1	99	Disintegrated						-	-	-	-	-	-
85	3.8	4.0	8.1	96	Disintegrated						11.8	460	0.5	1.2	2.4	61
55	3.8	6.7	16.7	89	Disintegrated						-	-	-	-	-	-
50	1.3	2.6	6.0	67	Disintegrated						18.3	535	0.6	1.4	2.4	51
50	2.2	3.3	5.5	97	Too weak to test						23.9	595	1.8	2.6	4.2	88
0	2.2	3.8	9.6	83	Disintegrated						-	-	-	-	-	-

TABLE 13 (Contd)

MECHANICAL PROPERTIES OF POLYURETHANE ELASTOMERS PREPARED
WITH DIFFERENT DI-ISOCYANATES BEFORE AND AFTER AGEING

Key:

TS	Tensile strength
EB	Extension at break
M_{100}, M_{200}, M_{300}	Moduli at extensions of 100, 200 and 300 per cent
H	Hardness
-	Value not recorded or too low to be accurately recorded

Code Number	Polyol	Di-isocyanate	Cross Linker/ Chain Extender	Original Properties (Unaged Controls)						28
				TS MN/m²	EB %	M_{100} MN/m²	M_{200} MN/m²	M_{300} MN/m²	H BS°	TS MN/m²
S 118	Polyether (Polyoxybutylene glycol)	TDI 100	TMP/MOCA	8.9	235	4.4	7.8	-	90	6.0
S 119		TDI 80/20	TMP/MOCA	16.9	345	3.0	5.3	9.9	89	13.7
S 120		TDI 65/35	TMP/MOCA	10.5	225	3.5	5.6	-	89	9.8
S 119A		TDI 80/20	TMP	2.9	180	1.5	-	-	76	3.9
S 121A		NDI	TMP/MOCA	3.9	120	3.5	-	-	90	-
S 121B		NDI	TMP	3.0	120	1.3	-	-	74	5.7
S 122A		MDI	TMP/MOCA	6.1	215	3.8	6.0	-	90	9.6
S 122B		MDI	TMP	4.2	250	0.6	2.0	-	67	3.9
S 123A		HDI	TMP/MOCA	13.6	460	0.8	0.8	1.6	65	6.7
S 124B		MDI mod	TMP	3.9	245	0.8	-	-	82	4.2
S 125A		MCI	TMP/MOCA	5.0	285	1.0	4.5	-	66	3.1
S 125B		MCI	TMP	0.7	280	0.1	0.6	-	39	2.0
S 126A		TMHDI	TMP/MOCA	5.6	430	0.3	0.8	1.5	57	1.3
S 127A		IDI	TMP/MOCA	15.9	445	0.7	1.8	3.1	64	5.5
S 133A		XDI	TMP/MOCA	18.8	565	1.3	1.9	3.1	82	5.7

r cent

ely recorded

Note: $6.9 \text{ MN/m}^2 = 1000 \text{ lb/in}^2$

nal Properties ged Controls)				28 Days Immersion in Water at 80°C						28 Days Immersion in STF at 65°C					
M_{100} MN/m²	M_{200} MN/m²	M_{300} MN/m²	H BS°	TS MN/m²	EB %	M_{100} MN/m²	M_{200} MN/m²	M_{300} MN/m²	H BS°	TS MN/m²	EB %	M_{100} MN/m²	M_{200} MN/m²	M_{300} MN/m²	H BS°
4.4	7.8	-	90	6.0	375	1.7	2.6	3.9	76	5.1	115	5.1	-	-	78
3.0	5.3	9.9	89	13.7	610	0.7	1.5	2.3	75	3.9	170	2.5	-	-	73
3.5	5.6	-	89	9.8	500	1.9	2.7	3.8	73	4.4	100	4.4	-	-	76
1.5	-	-	76	3.9	310	0.8	1.8	3.2	74	1.4	80	-	-	-	70
3.5	-	-	90	-	-	-	-	-	-	-	-	-	-	-	-
1.3	-	-	74	5.7	295	0.7	1.9	3.5	59	0.9	55	-	-	-	67
3.8	6.0	-	90	9.6	440	2.1	3.2	4.6	79	-	-	-	-	-	-
0.6	2.0	-	67	3.9	355	0.4	1.2	2.6	53	0.7	90	5.0	-	-	-
0.8	0.8	1.6	65	6.7	625	0.7	1.2	2.3	35	5.9	415	0.2	0.7	1.6	<30
0.8	-	-	82	4.2	435	0.2	0.8	1.2	53	0.5	130	0.4	-	-	40
1.0	4.5	-	66	3.1	330	0.8	1.5	2.6	55	1.9	170	0.7	-	-	37
0.1	0.6	-	39	2.0	500	0.2	0.6	1.2	28	-	-	-	-	-	-
0.3	0.8	1.5	57	1.3	485	-	-	0.2	41	1.1	265	0.1	0.6	-	<30
0.7	1.8	3.1	64	5.5	540	0.2	0.4	0.7	41	2.8	245	0.4	1.9	-	34
1.3	1.9	3.1	82	5.7	530	0.6	1.3	1.3	30	2.3	280	0.8	1.5	-	<30